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- First interlaboratory comparison of Mg isotopic data of geostandards
- Analysis of standards with composition ranging from ultramafic to felsic

Supporting Information:
- Supporting Information S1
- Table S1

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Interlaboratory comparison of magnesium isotopic compositions of 12 felsic to ultramafic igneous rock standards analyzed by MC-ICPMS

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Abstract To evaluate the interlaboratory mass bias for high-precision stable Mg isotopic analysis of natural materials, a suite of silicate standards ranging in composition from felsic to ultramafic were analyzed in five laboratories by using three types of multicollector inductively coupled plasma mass spectrometer (MC-ICPMS). Magnesium isotopic compositions from all labs are in agreement for most rocks within quoted uncertainties but are significantly (up to 0.3‰ in $^{26}Mg/^{24}Mg$, >4 times of uncertainties) different for some mafic samples. The interlaboratory mass bias does not correlate with matrix element/Mg ratios, and the mechanism for producing it is uncertain but very likely arises from column chemistry. Our results suggest that standards with different matrices are needed to calibrate the efficiency of column chemistry and caution should be taken when dealing with samples with complicated matrices. Well-calibrated standards with matrix elements matching samples should be used to reduce the interlaboratory mass bias.

1. Introduction

Recent advent of multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) has enabled high-precision analysis of stable Mg isotopes and makes it possible to explore Mg isotopic variations in natural samples and its potential applications in geochemistry and cosmochemistry [*Young and Galy*, 2004; *Ke et al.*, 2011]. Nevertheless, there are still debates on how Mg isotopes are distributed in planetary reservoirs, such as whether the Earth and chondrites have a similar Mg isotopic composition or not [*Teng et al.*, 2007; 2010a; *Wiechert and Halliday*, 2007; *Handler et al.*, 2009; *Yang et al.*, 2009; *Young et al.*, 2009; *Bourdon et al.*, 2010; *Chakrabarti and Jacobsen*, 2010; *Dauphas et al.*, 2010; *Schiller et al.*, 2010; *Huang et al.*, 2011; *Liu et al.*, 2011; *Pogge Von Strandmann et al.*, 2011; *Xiao et al.*, 2013]. *Wiechert and Halliday* [2007] and *Young et al.* [2009] found the Earth, as sampled by peridotite xenoliths, is isotopically (up to 0.3‰) heavier than chondrites. By contrast, *Teng et al.* [2007] and other studies [*Handler et al.*, 2009; *Yang et al.*, 2009; *Bourdon et al.*, 2010; *Chakrabarti and Jacobsen*, 2010; *Dauphas et al.*, 2010; *Schiller et al.*, 2010; *Teng et al.*, 2010a; *Huang et al.*, 2011; *Liu et al.*, 2011; *Pogge Von Strandmann et al.*, 2011; *Xiao et al.*, 2013], based on measurements of globally distributed peridotite xenoliths and oceanic basalts, suggested that the Earth and

chondrites have identical Mg isotopic composition at a precision of $\pm 0.07‰$ (2SD, δ^{26}Mg). These debates likely reflect analytical artifacts in high-precision Mg isotopic analysis by MC-ICPMS conducted in different laboratories because the difference in δ^{26}Mg between the Earth and chondrites as proposed by *Wiechert and Halliday* [2007] and *Young et al*. [2009] is $<0.3‰$ whereas the difference in δ^{26}Mg for certain USGS rock standards, such as BCR-1 and BCR-2, as well as San Carlos olivine, reported by different labs is up to $0.5‰$. For example, δ^{26}Mg varies from -0.58 to $-0.09‰$ for BCR-1 [*Young and Galy*, 2004; *Teng et al*., 2007; *Wiechert and Halliday*, 2007; *Huang et al*., 2009; *Bourdon et al*., 2010; *Chakrabarti and Jacobsen*, 2010], from -0.45 to $-0.12‰$ for BCR-2 [*Baker et al*., 2005; *Bizzarro et al*., 2005; *Teng et al*., 2007; *Tipper et al*., 2008; *Huang et al*., 2009; *Wombacher et al*., 2009; *Bourdon et al*., 2010; *Wasserburg et al*., 2012; *Shen et al*., 2013; *Wimpenny et al*., 2014a, 2014b], and from -0.55 to $-0.19‰$ for homogenous San Carlos olivine powder [*Young et al*., 2009; *Chakrabarti and Jacobsen*, 2010; *Liu et al*., 2010]. These variations are several times beyond typical quoted uncertainties although all these rock and mineral standards are expected to have homogeneous Mg isotopic compositions.

To achieve universal comparability for Mg isotopic data and enable assessment of accuracy of data from different laboratories, well-characterized Mg isotopic standards are thus needed. Although the Mg isotopic standard Cambridge-1 [*Galy et al*., 2003] has been widely analyzed in different labs, yielding similar δ^{26}Mg values within quoted uncertainties [*Galy et al*., 2003; *Pearson et al*., 2006; *Tipper et al*., 2006; *Black et al*., 2006, 2007, 2008; *Bolou-Bi et al*., 2009; *Young et al*., 2009; *Bourdon et al*., 2010; *Chakrabarti and Jacobsen*, 2010; *Li et al*., 2010; *Teng et al*., 2010a, 2010b; *Pogge Von Strandmann et al*., 2011], this Mg standard is made of pure Mg and needs no sample preparation, hence does not test sample preparation accuracy and reproducibility, as is required for natural samples. On the other hand, sample preparation processes, e.g., sample dissolution and column chemistry, have the greatest potential for introducing analytical artifacts because of the large Mg isotope fractionation during column chemistry and significant matrix effects during Mg isotope analysis by the standard-sample bracketing method. Therefore, the Mg yields during sample preparation must be near 100% and without matrix elements. Sample preparation processes thus are the most important steps to monitor. For this purpose, seawater has been proposed as a standard for high-precision Mg isotopic analysis because seawater has a homogenous Mg isotopic composition and needs sample preparation before Mg isotopic analysis [*Foster et al*., 2010; *Ling et al*., 2011, and references therein]. Nonetheless, the matrices of seawater are different from those of natural rock and mineral samples. Additional rock standards are thus needed for quality control and interlaboratory calibration.

2. Standard Samples

In this study, we reported Mg isotopic data analyzed by MC-ICPMS in five laboratories for 12 new rock standards with a wide range of matrices and chemical compositions. The 12 powdered standards, with each about 150 g, were acquired from National Research Center for Geoanalysis, China (http://igeo.cags.ac.cn/), with recommended major and trace elemental concentrations (supporting information Table S1). An aliquot (about 1–3 g) of each standard powder was transferred into a small sample tube (cleaned with diluted acid and Milli-Q water) by using a piece of weighing paper and delivered to different labs for interlaboratory comparison. Since all standards are from the same bottles, sample homogeneity is thus guaranteed.

These 12 standards vary in chemical composition from felsic to ultramafic, with SiO_2 ranging from 34.3 to 72.8 wt %, MgO ranging from 0.16 to 41.0 wt %, CaO ranging from 0.10 to 9.9 wt %, and Al_2O_3 ranging from 0.21 to 17.7 wt % (Table 1). The large chemical variation results in large matrix element/MgO variations, e.g., Al_2O_3/MgO ranging from 0.005 to 81 and CaO/MgO ranging from 0.002 to 3.7 (Figure 1), which makes them well suitable for quality control of sample preparation processes and interlaboratory calibration.

3. Analytical Methods

The 12 standard samples were analyzed in five laboratories by using various sample dissolution method, column chromatography, sample introduction system, and MC-ICPMS. A brief description is given below for methods used in each laboratory. Nonetheless, Mg isotopic data from all laboratories are reported in standard δ-notation in per mil relative to DSM-3 [*Galy et al*., 2003]:

Table 1. Selected Major Element Compositions of Geostandards Analyzed in This Study[a]

Sample Name	Rock Type	SiO_2 (wt %)	Al_2O_3 (wt %)	CaO (wt %)	MgO (wt %)	Al_2O_3/MgO	CaO/MgO
GBW07101	Ultramafic	34.34	0.67	0.10	41.03	0.02	0.002
GBW07102	Ultramafic	37.75	0.21	1.80	38.34	0.01	0.047
GBW07112	Gabbro	35.69	14.14	9.86	5.25	2.69	1.88
GBW07105	Basalt	44.64	13.83	8.81	7.77	1.78	1.13
GBW07122	Amphibolite	49.60	13.76	9.60	7.20	1.91	1.33
GBW07123	Diabase	49.88	13.21	7.83	5.08	2.60	1.54
GBW07109	Syenite	54.48	17.72	1.39	0.65	27.26	2.14
GBW07111	Granodiorite	59.68	16.56	4.72	2.81	5.89	1.68
GBW07104	Andesite	60.62	16.17	5.20	1.72	9.40	3.02
GBW07110	Trachyte	63.06	16.10	2.47	0.84	19.17	2.94
GBW07113	Rhyolite	72.78	12.96	0.59	0.16	81.00	3.69
GBW07103	Granite	72.83	13.40	1.55	0.42	31.90	3.69

[a]Major element data are from National Research Center for Geoanalysis, China (see Table S1 for complete major and trace elemental data).

$$\delta^{X}Mg = 10^3 \times \left\{ \frac{(^{X}Mg/^{24}Mg)_{sample}}{(^{X}Mg/^{24}Mg)_{DSM\text{-}3}} - 1 \right\},$$

where X refers to mass 25 or 26.

3.1. Magnesium Isotopic Analysis at the University of Arkansas, Fayetteville (UA)

Procedures for sample dissolution, column chemistry, and instrumental analysis are similar to those reported in previous studies [*Teng et al*., 2007, 2010a; *Yang et al*., 2009; *Li et al*., 2010; *Teng and Yang*, 2014]. A brief description is given below.

All rock standards were dissolved by using a combination of HF-HNO_3-HCl by following previously established procedure [*Teng et al*., 2007]. No residue was observed under microscope in the solution. In preparation for chromatographic separation, all sample solutions were evaporated to dryness, fluxed with concentrated HNO_3, and finally dissolved in 1N HNO_3.

Separation of Mg was achieved by cation exchange chromatography with Bio-Rad 200–400 mesh AG50W-X8 precleaned resin in 1N HNO_3 media by following a similar procedure as described in previous studies [*Teng et al*., 2007; *Yang et al*., 2009; *Li et al*., 2010]. Samples containing ~10 μg of Mg were loaded on the resin and eluted with 1N HNO_3. Column chromatography was repeated as required to separate Na, Al, K, Ca, and Fe from Mg and obtain a pure Mg solution. The whole-procedure blank is $<$10 ng, which represents $<$0.1% of Mg loaded on the column.

Magnesium isotopic compositions were analyzed by the sample-standard bracketing method using a *Nu Plasma* MC-ICPMS [*Teng and Yang*, 2014]. Purified sample solution (~300 ppb Mg in ~3% (*v*/*v*) or ~0.45N HNO_3 solution) was introduced into the plasma with a "wet" plasma using a Cinnabar spray chamber and a MicroMist microuptake glass concentric nebulizer from Glass Expansion. Magnesium isotopes were analyzed in a low-resolution mode, with ^{26}Mg, ^{25}Mg, and ^{24}Mg measured simultaneously in separate Faraday cups (H5, Ax, and L4). The typical signal is ~2.5–4.5 V/300 ppb Mg with an uptake rate of 100 μL/min.

3.2. Magnesium Isotopic Analysis at UC Davis (UCD)

Rock powders were dissolved using a mixture of concentrated HF-HNO_3 and heated at 140°C for 48 h. After evaporating to incipient dryness the samples were redissolved in concentrated HCl in order to prevent the formation of insoluble fluorides. The samples were then dried, redissolved in concentrated HNO_3, and small aliquots were removed (~20 μg of Mg) to be processed through column chemistry. Magnesium was purified from matrix elements and potential isobaric interferences using cation exchange chromatography in a method adapted from *Teng et al*. [2007]. Standards and unknowns were dissolved in 0.5 mL of 1N HNO_3 before eluting through 0.75 mL of BioRad AG50W-X12 resin (200–400 mesh). The column procedure was first calibrated in order to separate Mg from matrix elements such as Na, Al, K, Ti, Fe, and Ca. In particular, separation of Mg and Ca is important as the presence of Ca in sample solutions has been shown to cause fractionation of Mg isotope ratios by up to 1‰ [*Young and Galy*, 2004]. The Mg cut was collected in 12 mL of 1N HNO_3. Once eluted, the Mg fraction was dried down and the residue redissolved in 20 μL of

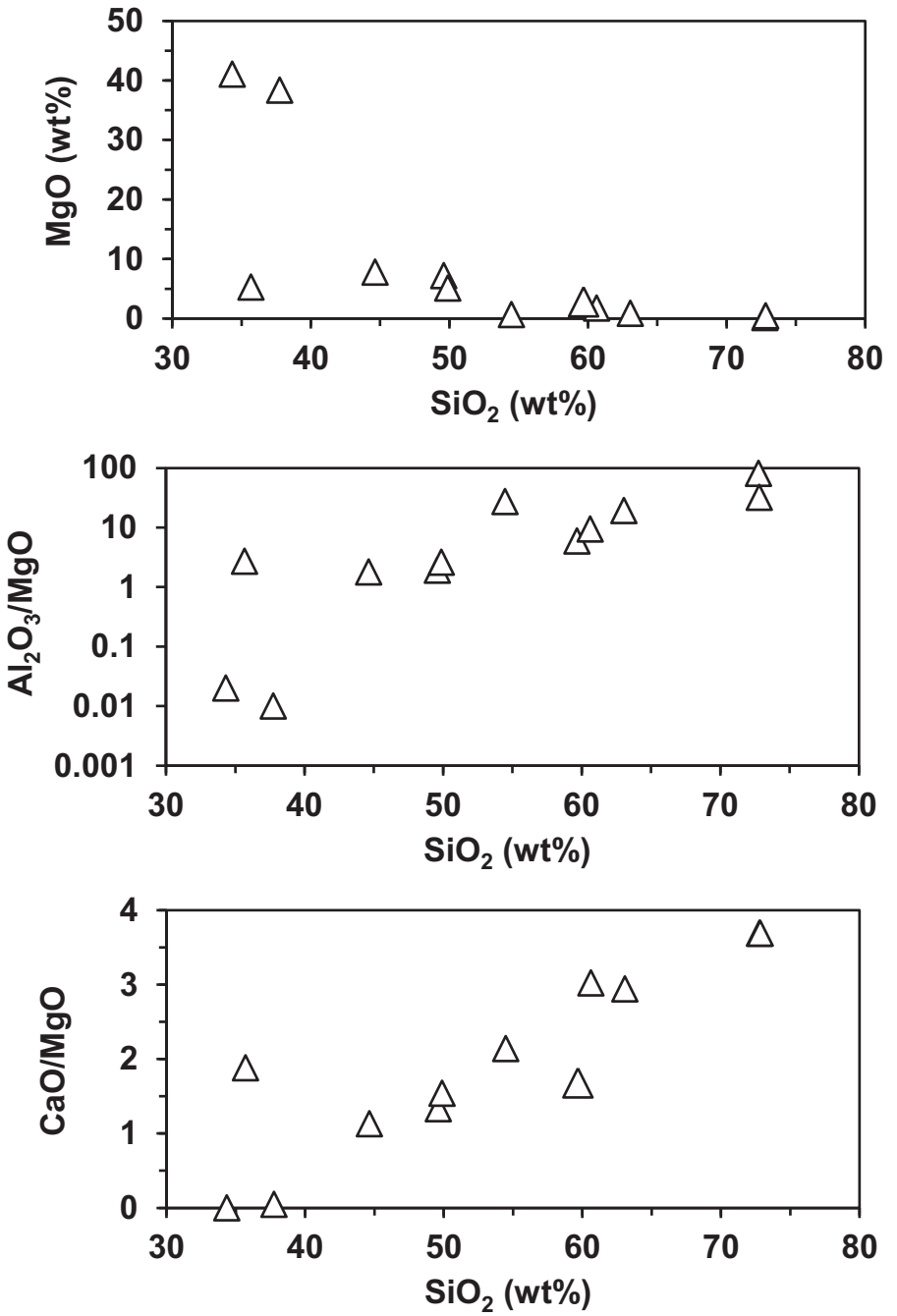

Figure 1. Variations of MgO, Al_2O_3/MgO, and CaO/MgO versus SiO_2 for standards investigated in this study. Data are reported in Table 1.

concentrated HNO_3 to oxidize any organic molecules derived from the resin. After repeating this column chemistry the final Mg fraction was dried down and redissolved in 1 mL of 2% HNO_3. Before and after sample processing the resin was cleaned by repeated elutions of 7N HNO_3 and MQ H_2O.

The Mg isotope ratios were measured on a ThermoFisher Scientific *Neptune Plus* HR-MC-ICP-MS in the Department of Earth and Planetary Sciences at the University of California at Davis. Isotopic analyses of Mg were bracketed using the DSM-3 pure Mg standard [*Galy et al.*, 2003] in order to account for instrumental mass bias and drift throughout the analysis period. Each sample was initially prescreened using 1% of the final Mg solution to ensure accurate dilution of the sample to match the signal intensity of the bracketing

standard to within 10%. Samples were analyzed under dry plasma conditions using an ESI Apex IR desolvating nebulizer which suppresses oxide interferences. The samples were analyzed in medium resolution to avoid the CN^+ peak on ^{26}Mg, which cannot be resolved at low resolution. Using a high sensitivity $\times$ skimmer cone, the typical intensities for a 500 ppb solution at medium resolution were between 20 and 25V of ^{24}Mg. Blank intensities on ^{24}Mg were typically 0.003–0.005V. To assess the accuracy of our measurements the pure Mg standard CAM-1 was routinely measured throughout each analytical session. In total, CAM-1 was measured 31 times with an average $\delta^{26}Mg$ value of $-2.62 \pm 0.07‰$, which is within error of the accepted value ($-2.59 \pm 0.14‰$) [*Galy et al*., 2003]. In order to assess the accuracy of the column chemistry and external reproducibility, the USGS basalt standards BCR-2 and BHVO-2 were processed with every batch of column chemistry and analyzed alongside the unknowns. On average, BCR-2 had a $\delta^{26}Mg$ value of $-0.17 \pm 0.06‰$ and $\delta^{25}Mg$ value of $-0.08 \pm 0.05‰$ (n = 12), while BHVO-2 had a $\delta^{26}Mg$ value of $-0.21 \pm 0.04‰$ and $\delta^{25}Mg$ value of $-0.11 \pm 0.05‰$ (n = 12). Both basalt standards are within error of the estimated average composition of the upper continental crust ($-0.22‰$) [*Li et al*., 2010] and other recent published values for basalts [e.g., *Pogge Von Strandmann et al*., 2008; *Handler et al*., 2009; *Bourdon et al*., 2010; *Teng et al*., 2010a].

3.3. Magnesium Isotopic Analysis at Freie Universität Berlin (FUB)

For 12 silicate materials, 10–25 mg of sample powder was used for Mg purification. For all materials two batches were digested. For samples GBW07103, GBW07109, GBW07110, and GBW07113, the second set of the second batch was not analyzed, however. The powders were reacted in closed Savillex Teflon beakers (15 mL volume) at 180°C for 10 h using 3 mL of a 1:2 mix of concentrated HF and concentrated HNO_3. The resulting solutions were treated with concentrated H_2O_2 to oxidize residual reduced carbon. In the next step, 0.2 mL of concentrated $HClO_4$ were added and the solutions were heated in the closed beakers at 120°C for 1 h to re-dissolve potential fluoride precipitates. The solutions were checked optically for solid residues and solutions free of precipitates were evaporated to dryness at 180°C. The dry residue was re-dissolved with 1 mL of 6N HCl and then evaporated at 90°C. Remaining traces of $HClO_4$ were then evaporated by heating at 180°C. The dry residues were then dissolved in 6N HCl and stored as stock solutions for Mg purification.

For Mg purification, 0.5 mL of the stock solutions containing $\geq$10 μg/g Mg in all cases was used. Iron was removed using Bio-Rad columns with 2 mL of anion exchange resin AG1 X8 (200–400 mesh) [*Wiechert and Halliday*, 2007]. Magnesium was eluted with 6N HCl while Fe was retained on the resin. In the second step, the solution was passed through ion exchange columns with 2.1 mL AG W50 X12 (200–400 mesh) using 2N HCl, resulting in the removal of Ca, K, and Al. In the third step, the solutions were passed through the same columns with 1.1N HCl as an eluent to remove Na and Ti. An additional fourth separation step for the removal of Mn for samples GBW07103, GBW07109, GBW07110, and GBW07113 was necessary due to high Mn/Mg ratios. The Mn separation was performed employing a protocol modified from *Wombacher et al*. [2009] using 2 mL of AG W50 X8 (100–200 mesh) in Bio-Rad columns and a 19:1 mix of Acetone and 9.55N HCl as eluent to remove Mn. The retained Mg was then eluted with 6N HCl. It is necessary to dissolve the residue from the third separation step in 25 μL of 9.55N HCl before the addition of 475 μL of acetone as the dry residues do not readily dissolve in a mixed acetone-HCl solution.

In order to access Mg yield during the column chemistry, splits were taken before and after the Mg cut during each column step and measured separately for Mg concentrations. Concentrations of Mg and potential contaminants were measured in the purified solutions and stock solutions for Mg isotope analysis were stored in 4 mL HDPE bottles. The procedure blank was determined to be 33 ng, equivalent to $<$0.1% of the Mg loaded on the columns for all materials apart from materials GWB07103, GWB07109, and GWB07113, for which this blank level represents up to 0.6% of the treated Mg. Magnesium recovery during column chemistry for standards GWB07101, GWB07102, GWB07104, GWB07105, GWB07111, GWB07112, GWB07122, and GWB07123, as estimated by comparing the total Mg in before and after-Mg cuts with Mg in the Mg cuts, was always better than 99.4% and usually around 99.9%. Magnesium recovery of materials GWB07103, GWB07109, GWB07110, and GWB07113 was typically $\sim$99%.

All samples and standards were diluted in 0.2N HNO_3 and closely matched to 100 ppb Mg ($\pm$10%). Isotope ratios were measured on a Neptune MC-ICP-MS at Deutsches GeoforschungsZentrum, Potsdam (Germany) using a standard-sample bracketing protocol with DSM-3 as the reference solution. Analyses were done in low-resolution mode using a Scott double pass cyclonic quartz spray chamber combined with a low flow

(50 μL/min) PFA nebulizer and a high sensitivity $\times$ skimmer cone (Ni). Magnesium isotopes were measured simultaneously, with ^{24}Mg on L2, ^{25}Mg on C, and ^{26}Mg on H3, respectively. Typical signal intensities of ^{24}Mg were 5–8 V. Also, 0.2N HNO_3 was measured before and after each sample and standard. The average of these measurements was used as analytical baseline to correct respective sample or standard.

The accuracy and reproducibility of the analyses were checked by multiple whole-procedure replicates of international reference materials BHVO-2, JB-2, BCR-1, SCo-1, Mag-1, UB-N, and PCC as well as in-house materials DAR (Peridotite), ASW (Alboran Sea water), and LWL-2 (tap water at the Department on Earth Sciences, Freie Universität Berlin). The external reproducibilities for δ^{25}Mg and δ^{26}Mg, determined using these reference materials, were found to be 0.06 and 0.10‰ (2 SD), respectively.

3.4. Magnesium Isotopic Analysis at Harvard University (Harvard)

Analytical procedures are similar to those described in *Chakrabarti and Jacobsen* [2010]. Approximately 20 mg of powdered samples were treated with mixtures of HF and HNO_3 acids (1:3) using Savillex teflon 15 mL screw-cap containers at 200°C for ~48 h followed by drydown in isolated Teflon chambers. The residue was then treated with 1:1 mixtures of concentrated HNO_3 and HCl and subsequently dried in the same way as above, followed by fluxing the residue with 0.5 mL of concentrated HNO_3. After complete dissolution, the samples were dried and redissolved in few milliliters of 1N HNO_3. One hundred to two hundred micro liter of this stock solution was inserted into the columns. The amount of Mg inserted into the columns for purification is typically less than 5 μg.

Separation and purification of Mg was performed by ion-exchange chromatography using 0.75 mL of Bio-Rad 50W-X12 (200–400 mesh) cation exchange resin in Savillex Teflon columns. The resin in each column was cleaned with 20 mL 8N HNO_3 acid and conditioned with 3 mL 1N HNO_3 prior to introduction of samples. Magnesium was eluted in 9 mL of 1N HNO_3. High yields (>99%) were ensured by collecting additional 1 mL aliquots before and after the 9 mL "Mg-cut" and by measuring the intensity of Mg in these "safety" aliquots relative to the Mg cut. To ensure complete separation of Mg from the other cations, all samples were passed through the columns twice. The concentration of any cation to that of Mg was <5%. Total procedural blanks for Mg are estimated to be less than 2 ng.

Magnesium isotope ratios were measured in the static mode using a GV IsoProbe-P MC-ICPMS. ^{24}Mg, ^{25}Mg, and ^{26}Mg were measured in Faraday cups L3, Ax, and H3, respectively. ^{27}Al was simultaneously monitored in cup H6. Purified Mg solutions (in 2% HNO_3) were introduced using an APEX-Q spray chamber fitted with an additional desolvator (ACM from Elemental Scientific Inc.) and a self-aspirating PFA nebulizer with an uptake rate of 100 μL/min. We used a combination of He (8 mL/min) and H_2 (3 mL/min) gases in the collision cell, a unique feature of the GV IsoProbe-P to get rid of potential isobaric molecular interferences (e.g., C_2^+ and CN^+) on all isotopes of Mg. All measurements were performed with a resolving power (R_{power} − 5%, 95%) of ~1100 [*Weyer and Schwieters*, 2003]. For all samples and standards, we used 150 ppb Mg solutions, which typically resulted in a 2.5–3.0 V signal on mass 24 with a 100 μL/min uptake rate and a 10^{11} Ω resistor and using standard Al sample and Ni skimmer cones.

Magnesium isotope ratios were measured by standard-sample bracketing to correct for instrumental mass bias. Each sample or standard was bracketed by measurements of the DSM-3 pure Mg metal standard [*Galy et al*., 2003]. To obtain a similar mass bias between the samples and the bracketing standard, it is important to match the concentrations of the standard and the sample solutions. Hence, for all our analyses, the concentration of the sample solution was adjusted to match that of the bracketing standard DSM-3 (150 ppb) within 10%. The internal precision for the ^{26}Mg/^{24}Mg and ^{25}Mg/^{24}Mg ratios in each measurement of 20 cycles with 10 s integration time is less than 50 and 25 ppm, respectively (2SE). Electronic baselines were measured before every sample or standard. Along with samples, the pure Mg standards Cambridge1 [*Galy et al*., 2003], Harvard-JM, Harvard-Spex, and Harvard-AA displaying a large range in δ^{26}Mg [*Chakrabarti and Jacobsen*, 2010] were also measured. All samples, except GBW07122, was analyzed in two different analytical sessions and the total number of measurements (calculated δ-values, w.r.t. DSM-3) are reported (N). Two standard deviation error bars are calculated based on total number of measurements per sample (N).

3.5. Magnesium Isotopic Analysis at the Bristol Isotope Group (BIG)

Procedures for sample analyses are similar to those described in previous studies [*Pogge von Strandmann*, 2008; *Foster et al*., 2010; *Pogge von Strandmann et al*., 2011, 2012]. A brief description is given below.

Table 2. Magnesium Isotopic Compositions of Geostandards Analyzed in This Study[a]

Lab	δ^{25}Mg	2SD	δ^{26}Mg	2SD	N
GBW07101, Ultramafic					
UA	−0.17	0.07	−0.33	0.10	4
UA	−0.19	0.06	−0.36	0.07	4
UA	−0.15	0.05	−0.27	0.09	4
UA	−0.19	0.06	−0.37	0.09	4
UA	−0.14	0.07	−0.28	0.09	4
UA	−0.16	0.09	−0.31	0.08	4
UA Ave.	−0.17	0.03	−0.32	0.03	
UCD	−0.12	0.01	−0.27	0.05	
FUB	−0.11	0.17	−0.19	0.31	4
Harvard	−0.10	0.08	−0.19	0.09	7
BIG	−0.13	0.06	−0.26	0.07	12
GBW07102, Ultramafic					
UA	−0.05	0.06	−0.12	0.09	4
UA	−0.07	0.05	−0.10	0.10	4
UA	−0.06	0.06	−0.13	0.09	4
UA	−0.05	0.06	−0.14	0.08	4
UA	−0.09	0.04	−0.16	0.08	4
UA	−0.05	0.07	−0.12	0.09	4
UA	−0.05	0.09	−0.13	0.08	4
UA Ave.	−0.07	0.02	−0.13	0.03	
UCD	−0.03	0.03	−0.10	0.05	
FUB	−0.12	0.08	−0.20	0.09	4
Harvard	−0.10	0.10	−0.20	0.16	5
BIG	−0.12	0.02	−0.23	0.03	8
GBW07112, Gabbro					
UA	−0.10	0.03	−0.20	0.05	4
UA	−0.09	0.06	−0.19	0.08	4
UA	−0.11	0.14	−0.24	0.14	4
UA	−0.10	0.05	−0.19	0.09	4
UA	−0.10	0.09	−0.18	0.08	4
UA Ave.	−0.10	0.02	−0.20	0.03	
UCD	−0.09	0.10	−0.15	0.10	
UCD	−0.06	0.01	−0.12	0.06	
UCD Ave.	−0.06	0.01	−0.13	0.05	
FUB	−0.09	0.03	−0.19	0.08	5
Harvard	−0.13	0.12	−0.27	0.15	3
GBW07105, Basalt					
UA	−0.20	0.04	−0.44	0.05	4
UA	−0.22	0.06	−0.39	0.08	4
UA	−0.24	0.05	−0.50	0.09	4
UA Ave.	−0.21	0.03	−0.44	0.04	
UCD	−0.20	0.04	−0.40	0.02	
UCD	−0.19	0.04	−0.36	0.08	
UCD Ave.	−0.19	0.03	−0.40	0.02	
FUB	−0.23	0.08	−0.47	0.09	5
Harvard	−0.24	0.12	−0.49	0.15	5
BIG	−0.18	0.04	−0.35	0.04	8
GBW07122, Amphibolite					
UA	−0.07	0.06	−0.14	0.09	4
UA	−0.09	0.06	−0.20	0.09	4
UA	−0.12	0.04	−0.19	0.08	4
UA	−0.11	0.07	−0.21	0.09	4
UA Ave.	−0.10	0.03	−0.18	0.04	
UCD	−0.08	0.04	−0.19	0.03	
FUB	−0.07	0.04	−0.16	0.04	5
Harvard	−0.22	0.08	−0.44	0.20	3
GBW07123, Diabase					
UA	−0.13	0.06	−0.28	0.08	4
UA	−0.13	0.06	−0.32	0.09	4
UA	−0.15	0.07	−0.26	0.09	4
UA Ave.	−0.14	0.04	−0.28	0.05	
UCD	−0.07	0.02	−0.14	0.02	
UCD	−0.06	0.04	−0.14	0.05	
UCD Ave.	−0.07	0.02	−0.14	0.02	
FUB	−0.13	0.10	−0.23	0.16	6
Harvard	−0.17	0.09	−0.33	0.09	4

Table 2. (continued)

Lab	δ^{25}Mg	2SD	δ^{26}Mg	2SD	N
GBW07109, Syenite					
UA	−0.16	0.05	−0.31	0.09	4
UA	−0.15	0.01	−0.27	0.05	4
UA	−0.15	0.04	−0.30	0.08	4
UA	−0.19	0.06	−0.39	0.09	4
UA Ave.	−0.15	0.01	−0.30	0.03	
UCD	−0.11	0.05	−0.22	0.06	
FUB	−0.12	0.06	−0.21	0.06	3
GBW07111, Granodiorite					
UA	−0.14	0.03	−0.25	0.05	4
UA	−0.10	0.06	−0.20	0.08	4
UA	−0.17	0.02	−0.26	0.04	4
UA	−0.15	0.05	−0.29	0.09	4
UA	−0.10	0.04	−0.26	0.08	4
UA	−0.12	0.09	−0.20	0.08	4
UA Ave.	−0.15	0.01	−0.25	0.03	
UCD	−0.09	0.10	−0.15	0.10	
FUB	−0.14	0.02	−0.27	0.05	6
Harvard	−0.14	0.10	−0.28	0.12	5
GBW07104, Andesite					
UA	−0.32	0.04	−0.61	0.05	4
UA	−0.33	0.06	−0.62	0.08	4
UA	−0.33	0.06	−0.67	0.09	4
UA	−0.32	0.04	−0.63	0.06	4
UA	−0.39	0.04	−0.72	0.08	4
UA	−0.36	0.09	−0.72	0.08	4
UA Ave.	−0.34	0.02	−0.65	0.03	
UCD	−0.36	0.09	−0.67	0.05	
FUB	−0.39	0.05	−0.77	0.09	7
Harvard	−0.32	0.10	−0.64	0.15	4
GBW07110, Trachyte					
UA	0.04	0.05	0.07	0.10	4
UA	0.04	0.06	0.08	0.08	4
UA	0.08	0.06	0.09	0.09	4
UA	0.03	0.19	0.10	0.08	4
UA	0.05	0.06	0.07	0.07	2
UA Ave.	0.05	0.03	0.08	0.04	
UCD	0.06	0.03	0.10	0.05	
FUB	0.02	0.01	0.07	0.03	5
Harvard	−0.01	0.10	−0.02	0.15	4
GBW07113, Rhyolite					
UA	−0.19	0.06	−0.32	0.08	4
UA	−0.26	0.05	−0.47	0.09	4
UA	−0.28	0.09	−0.45	0.09	4
UA	−0.21	0.04	−0.44	0.08	4
UA Ave.	−0.22	0.03	−0.42	0.04	
UCD	−0.24	0.03	−0.46	0.03	
UCD	−0.28	0.05	−0.48	0.03	
UCD Ave.	−0.25	0.02	−0.47	0.02	
FUB	−0.24	0.12	−0.45	0.25	4
GBW07103, Granite					
UA	−0.12	0.07	−0.25	0.16	4
UA	−0.16	0.05	−0.27	0.09	4
UA	−0.17	0.05	−0.23	0.02	4
UA	−0.14	0.04	−0.25	0.08	4
UA	−0.13	0.09	−0.27	0.08	4
UA Ave.	−0.15	0.02	−0.24	0.02	
UCD	−0.09	0.04	−0.18	0.06	
FUB	−0.12	0.12	−0.24	0.17	3
BIG	−0.15	0.06	−0.31	0.06	8

[a]UA = University of Arkansas laboratory; UCD = UC Davis laboratory; FUB = Freie Universität Berlin laboratory; Harvard = Harvard University laboratory; BIG = Bristol Isotope Group. UA Ave. = weighted mean and 2SD of data analyzed from UA over 3 years. UCD Ave. = weighted mean and 2SD of data analyzed from UCD. N = times of duplicate analysis during a session except N = times of replicate analysis through whole column preparation for FUB samples.

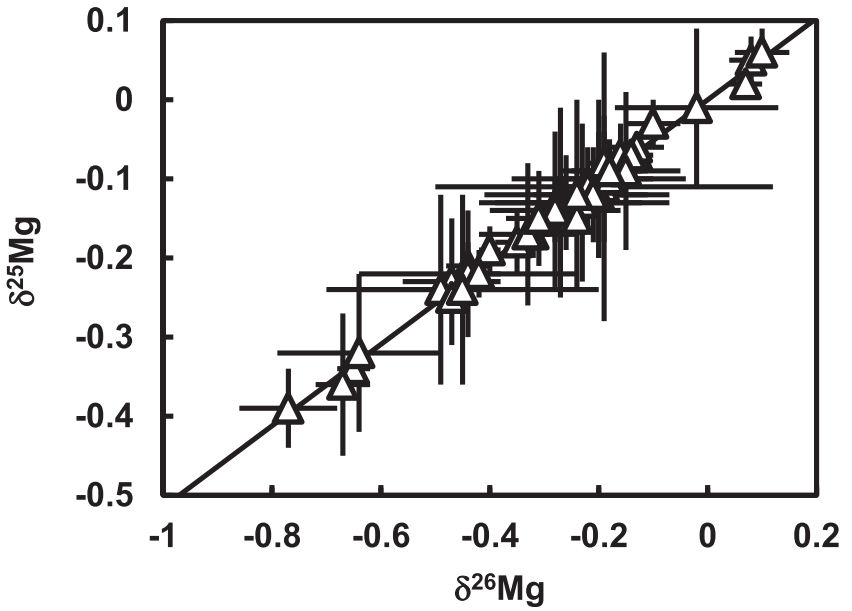

Figure 2. Magnesium three-isotope plot of standards investigated in this study. The solid line represents the fractionation line with a slope of 0.515. Data are reported in Table 2.

All sample powders were dissolved in stages of concentrated HF-HNO_3, followed by HNO_3, and finally HCl, using Savillex beakers. Following dissolution, the sample was dissolved in 2N HNO_3, and a small aliquot was taken for column chemistry. Splits of the elution were collected before and after the Mg collection bracket, to ensure as close to 100% Mg yield as possible was achieved. This showed that yields of >99.9% Mg were achieved.

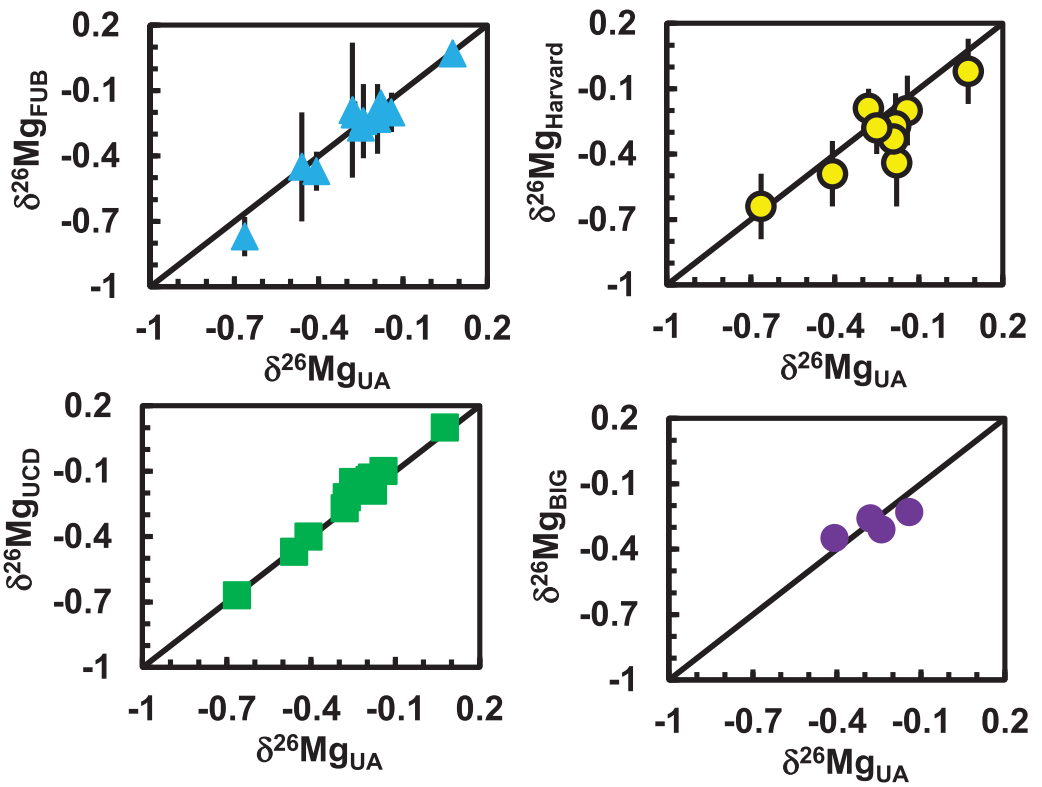

Figure 3. Comparison of Mg isotopic data measured in different laboratories. Data are reported in Table 2.

Table 3. Recommended Weighted Mean Mg Isotopic Compositions and 2SD of Geostandards Analyzed in This Study

Sample Name	Rock Type	δ^{25}Mg	2SD	δ^{26}Mg	2SD
GBW07101	Ultramafic	−0.12	0.01	−0.28	0.02
GBW07102	Ultramafic	−0.08	0.01	−0.14	0.02
GBW07112	Gabbro	−0.07	0.01	−0.18	0.02
GBW07105	Basalt	−0.20	0.02	−0.41	0.01
GBW07122	Amphibolite	−0.10	0.02	−0.18	0.02
GBW07123	Diabase	−0.09	0.02	−0.19	0.01
GBW07109	Syenite	−0.15	0.01	−0.27	0.02
GBW07111	Granodiorite	−0.15	0.01	−0.25	0.02
GBW07104	Andesite	−0.35	0.02	−0.66	0.02
GBW07110	Trachyte	0.03	0.01	0.08	0.02
GBW07113	Rhyolite	−0.24	0.02	−0.46	0.02
GBW07103	Granite	−0.14	0.02	−0.24	0.02

Magnesium purification was performed by a two-stage cation exchange chemistry, using Bio-Rad AG50W-X12 (200–400 mesh) precleaned resin in 2N HNO_3, as described by *Pogge von Strandmann et al*. [2011]. The total procedural blank for Mg isotope analysis by this method is ~0.4 ng Mg, which is insignificant compared to the 2–3 μg of Mg put through chemistry.

Magnesium isotope compositions were analyzed using a Neptune MC-ICP-MS, with a sample-standard bracketing system, relative to the standard DSM-3 [*Galy et al*., 2003]. Purified sample solution of ~100 ng/mL Mg was introduced via an Elemental Scientific Inc. ApexQ, with a ~50 μL/min uptake rate nebulizer tip, in 2% HNO_3. Mg isotopes were analyzed in low-resolution mode, with all isotopes measured simultaneously in separate Faraday cups (H3, Centre, L3). Each individual measurement consisted of 20 ratios (84 s total integration time). Each sample was analyzed 4 times during the same session (336 s/sample), with analyses separated by several hours. The typical signal is 18–20 V/100 ppb Mg with an uptake rate of 50 μL/min, using high-sensitivity × Ni skimmer cones [*Pogge von Strandmann et al*., 2011]. USGS and JGS silicate standard results by this method are documented in *Pogge von Strandmann et al*. [2011], seawater results by *Foster et al*. [2010], and carbonates by *Pogge von Strandmann* [2008]. Typical long-term external analytical precision, based on several years of repeated analyses of rock standards, is ±0.06‰ on δ^{26}Mg.

4. Results and Discussion

Magnesium isotopic data of these 12 standards measured by different labs are reported in Table 2 and all fall on the mass-dependent line with a slope of 0.515 (Figure 2). Overall, δ^{26}Mg of 12 standards ranges >0.8‰ and varies from −0.77‰ in an andesite standard (GBW07104) to +0.10‰ in a trachyte standard (GBW07110) (Figure 3).

The recommended Mg isotopic compositions for these 12 standards (Table 3), after excluding data that fall out of 1 SD of the mean of all other data, are calculated by using the following equations:

$$\textit{weighted mean} = \frac{\sum \frac{\overline{x}}{\sigma^2}}{\sum \frac{1}{\sigma^2}} \quad \textit{variation on mean} = \sqrt{\frac{1}{\sum \frac{1}{\sigma^2}}}$$

where $\overline{x}$ = mean Mg isotopic composition of a standard and σ is one standard deviation.

The overall variation in the recommended δ^{26}Mg value varies from −0.66‰ in an andesite standard (GBW07104) to 0.08‰ in the trachyte standard (GBW07110) (Table 3). The petrogenesis of these standard samples are not clear but their Mg isotopic compositions fall within the range of crustal and mantle rocks [*Teng et al*., 2007; *Wiechert and Halliday*, 2007; *Handler et al*., 2009; *Shen et al*., 2009, 2013; *Yang et al*., 2009; *Young et al*., 2009; *Bourdon et al*., 2010; *Chakrabarti and Jacobsen*, 2010; *Dauphas et al*., 2010; *Li et al*., 2010; *Liu et al*., 2010; *Schiller et al*., 2010; *Teng et al*., 2010a; *Huang et al*., 2011; *Liu et al*., 2011; *Pogge Von Strandmann et al*., 2011; *Telus et al*., 2012; *Yang et al*., 2012; *Huang et al*., 2013; *Xiao et al*., 2013; *Wimpenny et al*., 2014a, 2014b].

The interlaboratory difference in δ^{26}Mg for these 12 standards varies from 0.05‰ for the rhyolite standard (GBW07113) to 0.28‰ for the amphibolite standard (GBW07122) although data from all labs were in

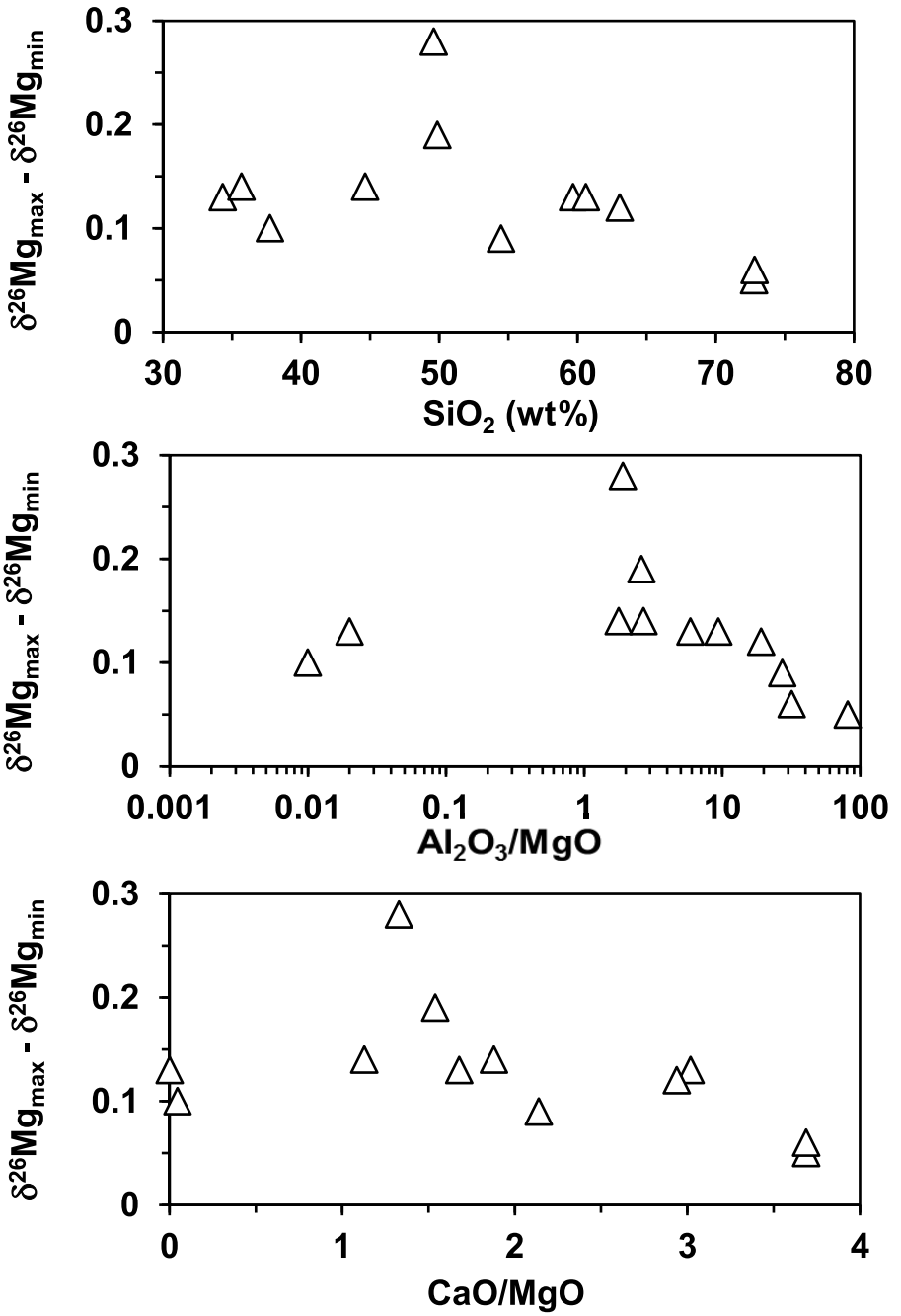

Figure 4. Maximum difference in δ^{26}Mg ($\delta^{26}Mg_{max} - \delta^{26}Mg_{min}$) versus SiO_2, Al_2O_3/MgO, and CaO/MgO for standards investigated in this study. Data are reported in Tables 1 and 2.

agreement within quoted uncertainties (Figure 3). When plotted against major elemental compositions, the interlaboratory mass bias (i.e., $\delta^{26}Mg_{max} - \delta^{26}Mg_{min}$) among these five labs does not correlate with SiO_2 content and matrix element/Mg ratios (e.g., CaO/MgO and Al_2O_3/MgO) (Figure 4). The sample that displays the largest interlaboratory mass bias is an amphibolite with moderate matrix elements (Table 2). Most of the difference for the amphibolite is due to a single δ^{26}Mg value. If this single Mg isotope ratio is excluded, then the interlaboratory difference reduces to 0.03‰. Overall, although the reason for these small interlaboratory differences is unknown, it most likely arises from column chemistry such as incomplete separation of matrix elements, low Mg yields, contamination of both samples and/or standards during sample

preparation, high procedural blank, etc. Additional process such as incomplete sample dissolution, e.g., the loss of fluorides during sample dissolution could also play a minor role.

This interlaboratory comparison study demonstrated that accuracy had to be assured for high-precision Mg isotopic analysis. Standards with different matrices need to be used to calibrate methods since methods working for high-Mg samples may not work for low-Mg ones. Cautions should be taken when dealing with samples with low MgO and complicated matrices. Well-calibrated standards matching sample matrixes should be used to reduce the interlaboratory mass bias in future studies.

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